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REACTIONS OF SILYL ENOL ETHERS AND KETENE SILYL KETALS WITH ISOCYANATES

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Summary

The reaction of silyl enol ethers with aryl isocyanates gave 2-siloxycycloalk-1-enecarboxamides or 4-siloxyazetidin-2-ones, depending on the structure of silyl enol ethers. On the other hand, ketene silyl ketals reacted with isocyanates to afford 2-(*N*-silylcarbamoyl)alkanoates or 4-siloxy-4-alkoxyazetidin-2-ones dependent upon the structure of isocyanates. These adducts were easily desilylated to the corresponding 2-carbamoylalkanones or 2-carbamoylalkanoates.

Introduction

Recent developments in the reactions of silyl enol ethers derived from aldehydes, ketones, and esters have been showing that these versatile compounds provide tremendous potential as enol equivalents for organic synthesis [1]. For instance, silyl enol ethers are good precursors of directed enolates for alkylation [2] or of quarternary ammonium enolates for regiospecific alkylation [3]. Titanium tetrachloride promoted Cross—Aldol reactions [4] and Michael reactions [5] of silyl enol ethers can serve as mild methods for the preparation of 3-hydroxy ketones and 1,5-diketones, respectively. The reactions of ketene silyl ketals with carbonyl compounds in the presence of titanium tetrachloride [6] or at rather high temperatures without an activating agent [7] can lead to 3-hydroxy esters. However, little is known about the reaction of silyl enolates with heterocumulenes: the reaction of ketene silyl ketals with ketene is sole example [8], and there have been no reports on the reactions of silyl enolates with isocyanates.

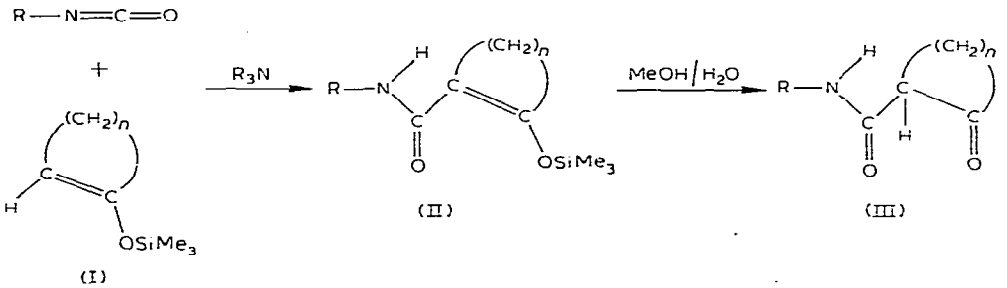
We have found that (i) the reactions of silyl enol ethers with isocyanates afford 2-siloxycycloalk-1-enecarboxamides or 4-siloxyazetidin-2-ones, depending upon the structure of the silyl enol ethers [9], and (ii) the corresponding reaction of ketene silyl ketals gave 2-(*N*-silylcarbamoyl)alkanoates or 4-siloxyazetidin-2-ones depending on the kind of isocyanates. We provide here a full

account of our research on the reactivity of silyl enol ethers and ketene silyl ketals toward isocyanates.

Results and discussion

The reactions of silyl enol ethers with isocyanates

The reactions of silyl enol ethers (I) derived from cyclopentanone and cyclohexanone with aryl isocyanates were found to take place in the presence of a catalytic amount of tertiary amine, such as triethylamine or pyridine, at 130—160°C to afford 2-siloxycycloalk-1-enecarboxamides (II) in good yield. The structure of II was confirmed on the basis of their NMR and IR spectra. Namely, the IR spectra of IIa—IIe display an NH stretching band, amide I and amide II band, and C=C stretching band, and their NMR spectra show the signals ascribed to the NH proton and the protons of the trimethylsilyl group. These adducts were easily hydrolyzed by using aqueous methanol to give N-aryl-2-oxocycloalkanecarboxamides, III, in almost quantitative yields. The results are summarized in Table 1. Spectral data of II and III are listed in Table 2.



(a: R = Ph, n = 3; b: R = Ph, n = 4; c: R = α-Np, n = 3; d, R = α-Np, n = 4; e: R = p-ClC6H4, n = 3)

It has been shown that an enamine which has a β-hydrogen reacts with isocyanates through nucleophilic addition to afford *N*-substituted 2-oxoalkanecarboxamides after hydrolysis [10], whereas vinyl ethers are unreactive toward aliphatic, aromatic and benzoyl isocyanates [11]. Consequently, cyclic silyl

TABLE 1

N-ARYL-2-OXOCYCLOALKANECARBOXAMIDES (III) OBTAINED IN THE REACTION OF CYCLIC SILYL ENOL ETHERS WITH ARYL ISOCYANATES FOLLOWED BY HYDROLYSIS

Compound	R	*n*	Conditions	Yield (%)	M.p. (°C)
IIIa	C_6H_5	3	130°C, 12 h	94	102—104 [a]
IIIb	C_6H_5	4	160°C, 24 h	72	105—107 [b]
IIIc	α-$C_{10}H_7$	3	130°C, 12 h	97	101—103 [c]
IIId	α-$C_{10}H_7$	4	160°C, 24 h	83	168—170 [d]
IIIe	p-ClC_6H_4	3	140°C, 12 h	95	118—119 [e]

[a] Lit. [12] 102—104°C. [b] Lit. [12] 106—108°C. [c] Lit. [17] 102.5—103.5°C. [d] Sufficient elemental analyses were obtained (see Experimental). [e] Lit. [17] 119°C.

TABLE 2

SPECTRAL DATA FOR *N*-ARYL-2-SILOXYCYCLOALK-1-ENECARBOXAMIDES (II) AND *N*-ARYL-2-OXOCYCLOALKENECARBOXAMIDES (III)

	IR (cm^{-1}) [a]					NMR (δ, ppm) [b]	
	ν(NH)	ν(C=O)	ν(Amide I)	ν(C=C)	ν(Amide II)	$SiCH_3$	NH
IIa	3360		1650	1625	1530	0.40	8.96
IIb	3380		1665	1635	1530	0.32	9.33
IIc	3290		1665	1630	1545	0.35	9.33
IId	3290		1660	1630	1545	0.23	9.77
IIe	3330		1660	1625	1525	0.39	9.00
IIIa	3200	1735	1665, 1645		1545		8.99
IIIb	3300	1710	1650		1530		9.50
IIIc	3200	1735	1660, 1640		1545		10.00
IIId	3180	1700	1655, 1635		1530		9.95
IIIe	3190	1735	1655, 1635		1535		8.77

[a] Measured as KBr disk. [b] Measured in $CDCl_3$.

enol ethers, like enamines, behave as nucleophilic reagents and can be used in place of the corresponding enamines such as morpholinocyclohexene [12].

Alkyl isocyanates such as methyl or cyclohexyl isocyanate did not react with silyl enol ethers at all under conditions similar to those employed in the case of aryl isocyanates.

On the other hand, when *p*-toluenesulfonyl isocyanate was employed as substrate, two types of addition reaction were observed to occur, depending upon the structure of silyl enol ethers. Cyclic silyl enol ethers (I) reacted with the isocyanate to give *N*-(*p*-toluenesulfonyl)-2-trimethylsiloxycycloalk-1-enecarboxamides (IV) through the enamine-type nucleophilic addition, while open

TABLE 3

N-(*p*-TOLUENESULFONYL)-2-OXOCYCLOALKANECARBOXAMIDES (V) AND *N*-(*p*-TOLUENESULFONYL)-2-OXOALKANECARBOXAMIDES (VIII) OBTAINED IN THE REACTION OF SILYL ENOL ETHERS WITH *p*-TOLUENESULFONYL ISOCYANATE FOLLOWED BY METHANOLYSIS

Compound	Conditions	Yield (%)	M.p. (°C)	Analysis (found (calcd.) (%))			
				C	H	N	S
Va	r.t., 15 min	95	93—94	55.32 (55.50)	5.49 (5.37)	4.97 (4.98)	11.33 (11.40)
Vb	r.t., 15 min	90	143—145 [a]				
VIIIa	r.t., 15 min	98	122—123	56.64 (56.55)	6.25 (6.44)	4.61 (4.71)	10.71 (10.78)
VIIIb	r.t., 15 min	98	116—117	60.55 (60.55)	4.47 (4.76)	4.35 (4.41)	10.20 (10.10)
VIIIc	r.t., 15 min	80	93—94	53.48 (53.52)	5.51 (5.61)	5.06 (5.20)	11.96 (11.91)
VIIId	r.t., 15 min	88	106—107	56.84 (56.55)	6.33 (6.44)	4.66 (4.71)	10.58 (10.78)
VIIIe	r.t., 15 min	92	127—128	62.72 (62.59)	5.48 (5.54)	3.93 (4.06)	9.39 (9.28)

[a] Lit. [12] 125—127°C.

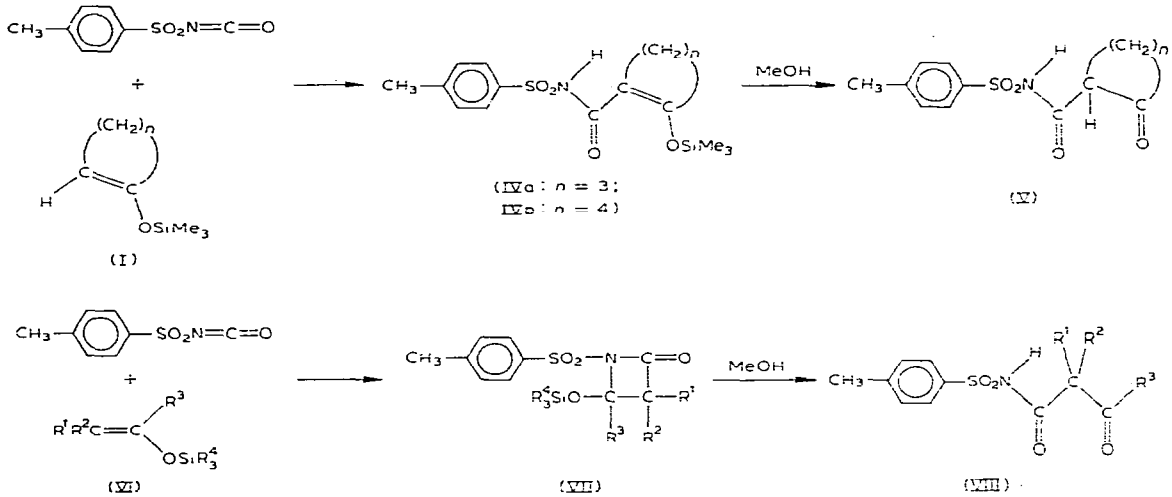
TABLE 4

SPECTRAL DATA FOR *N*-(*p*-TOLUENESULFONYL)-2-SILOXYCYCLOALK-1-ENECARBOXAMIDES (IV) AND 1-(*p*-TOLUENESULFONYL)-4-SILOXY-AZETIDIN-2-ONES (VII) AND THEIR METHANOLYSIS PRODUCTS, V AND VIII

Compound	IR (cm^{-1}) [a]					NMR (δ, ppm) [b]						Keto/enol
	ν(NH)	ν(C=O)	ν(Amide I)	ν(C=C)	ν(Amide II)	$SiCH_3$	^3CH [c]	NH	OH	Methylene or methine	vinylic proton	
IVa	3250	—	1670	1610	1430	0.33	—	9.57	—	—	—	—
IVb	3290	—	1675	1625	1430	0.40	—	10.15	—	—	—	—
VIIa	—	1710 [d]	—	—	—	—	4.10 [e]	—	—	—	—	—
VIIb	—	1695 [d]	—	—	—	0.17	4.44 [e]	—	—	—	—	—
VIIc	—	1730 [d]	—	—	—	0.18	4.52 [e]	—	—	—	—	—
VIId	—	1730 [d]	—	—	—	—	4.03, 4.47 [e]	—	—	—	—	—
VIIe	—	1725 [d]	—	—	—	—	5.01, 5.17 [e]	—	—	—	—	—
Va	3230	1735	1710	—	1460	—	—	9.47	—	3.10	—	100/0
Vb	3260	1660		—	1430	—	—	8.43	13.63	—	—	0/100
VIIIa	3220	1720	1690	—	1460	—	—	9.10, 10.07	13.38	3.67	5.27	72/25
VIIIb	3210	1645	1625	—	1460	—	—	9.12, 10.30	13.32	3.05	5.78	65/35
VIIIc	3220	1735	1705	—	1460	—	—	9.55	—	3.45	—	100/0
VIIId	3230	1730	1700	—	1430	—	—	9.56	—	3.20	—	100/0
VIIIe	3170	1710	1690	—	1450	—	—	9.55	—	3.73	—	100/0

[a] Measured as KBr disk. [b] Measured in $CDCl_3$. [c] ^3CH ring proton of azetidin-2-one. [d] Measured as neat liquid. [e] Measured in CCl_4.

chain silyl enol ethers (VI) afforded 1-(*p*-toluenesulfonyl)-4-trimethylsiloxyazetidin-2-ones (VII) through 1,2-cycloaddition. The structures of the adducts were elucidated on the basis of their NMR and IR spectra. The IR spectrum of IV displays NH stretching, amide I and amide II, and C=C stretching bands, and in its NMR spectrum are observed two singlets due to the trimethylsilyl group and the NH proton. On the other hand, the IR spectrum of VII shows no absorption band due to NH stretching, but displays a C=O stretching band due to the β-lactam carbonyl, and its NMR spectrum displays signals assigned to the trimethylsilyl group and β-lactam ring proton. The adducts, IV and VII, were easily desilylated to give the corresponding *N*-(*p*-toluenesulfonyl)-2-oxocycloalkanecarboxamides (V) and *N*-(*p*-toluenesulfonyl)-2-oxoalkanecarboxamides (VIII), respectively. Results and physical properties and analytical data are summarized in Table 3. Spectral data for the desilylated products (V and VIII) are listed in Table 4.



(a : $R^1 = R^2 = H$, $R^3 = C(CH_3)_3$, $R^4_3 = (C_2H_5)_3$;
b : $R^1 = R^2 = H$, $R^3 = C_6H_5$, $R^4_3 = (CH_3)_3$;
c : $R^1 = H$, $R^2 = R^3 = CH_3$, $R^4_3 = (CH_3)_2(C_2H_5)$;
d : $R^1 = H$, $R^2 = CH(CH_3)_2$, $R^3 = CH_3$, $R^4_3 = (C_2H_5)_3$;
e : $R^1 = H$, $R^2 = C_6H_5CH_2$, $R^3 = CH_3$, $R^4_3 = (C_2H_5)_3$)

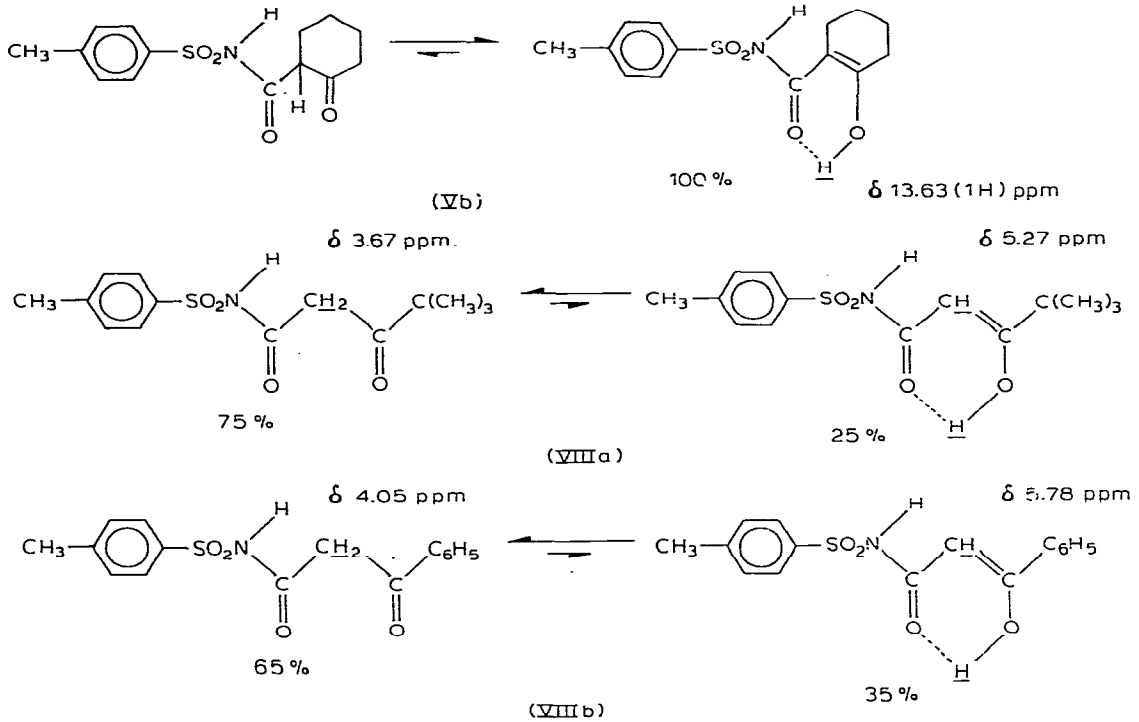
A keto—enol tautomerism of the *N*-sulfonyloxoalkanecarboxamides, V and VIII, can be observed by means of NMR spectroscopy. An enol proton of *N*-(*p*-toluenesulfonyl)-2-oxocyclohex-1-enecarboxamide (Vb) appears at δ 13.63 ppm (s, 1H) and its IR spectrum displays only one absorption band due to C=O stretching at 1660 cm^{-1}. Thus, Vb may be present only in the enol form, while the keto form is found to be rather stable in the case of VIIIa and VIIIb on the basis of their NMR spectra. The keto—enol ratio is calculated from the integration of the NMR peak areas of methylene protons of the keto form and the methine proton of the enol form, and is shown in Table 4. In other cases, the keto form seems to be far more stable than the enol form, so that any evidence for the presence of the enol form cannot be obtained.

TABLE 5

2-CARBAMOYLALKANOATES, X, XIII AND XV, OBTAINED IN THE REACTION OF KETENE SILYL KETALS WITH ISOCYANATES

Compound	R	R^1	R^2	Conditions	B.p. (°C/Torr) or m.p. (°C)	Yield [a] (%)	IR (cm^{-1}) [b]			NMR (δ, ppm) [c]
							ν(C=O)	ν(Amide I)	$\nu(SiCH_3)$	$SiCH_3$
Xa	p-ClC_6H_4	$-CH_2CH_2-$		r.t., 3 h	70–73	68(90)	1765	1660	1255 [d]	0.22, 0.33
Xb	$CH_2=CHCH_2$	$-CH_2CH_2-$		r.t., 24 h	135/0.18	27(90)	1770	1640	1250	0.24, 0.25
Xc	CH_3	$-CH_2CH_2-$		r.t., 24 h	110/0.25	30(95)	1775	1640	1250	0.27, 0.33
XIIIa	p-ClC_6H_4	CH_3	CH_3	45°C, 45 h	108/0.25	69(87)	1750	1660	1255	−0.05
XIIIb	C_6H_5	CH_3	CH_3	85°C, 24 h	88/0.22	58(83)	1745	1655	1250	−0.20
XIIIc	C_6H_5	H	CH_3	60°C, 30 h	100/0.45	58(86)	1750	1665	1250	0.23
XVa	Tosyl [e]	H	C_6H_5	r.t., 15 min	oil	−(97)	1750	—	1250	0.15 [f]
XVb	Tosyl [e]	H	CH_3	r.t., 15 min	oil	−(97)	1755	—	1255	0.23 [g]
XVc	Tosyl [e]	CH_3	CH_3	r.t., 15 min	oil	−(96)	1750	—	1255	0.34
XVd	Tosyl [e]	$-(CH_2)_5-$		r.t., 15 min	oil	−(99)	1745	—	1255	0.37

[a] Isolated yield. The values in parentheses are the yields of XI, XIV and XVI obtained by direct methanolysis of the reaction mixture. [b] Measured as neat liquid. [c] Measured in $CDCl_3$. [d] Measured as KBr disk. [e] Tosyl = p-$CH_3C_6H_4SO_2$. [f] ^3CH ring proton appeared at δ 5.99(s) ppm. [g] ^3CH ring proton appeared at δ 4.65 ppm (quartet, J 7 Hz).



The reaction of ketene silyl ketals with isocyanates

The reaction of a cyclic ketene silyl ketal (IX) derived from γ-butyrolactone with *p*-chlorophenyl isocyanate took place exothermally at ambient temperature to afford 2-(*N*-silylcarbamoyl)-γ-butyrolactone (Xa) in 68% yield. The ketene silyl ketal (IX) also reacted with alkyl isocyanates such as allyl or methyl isocyanate to give the same type of adducts (Xb and Xc). The observation that 4,5-dihydro-2-trimethylsiloxyfuran (IX) is reactive enough to react with alkyl isocyanates, stands in sharp contrast to the fact that neither silyl enol ethers (vide supra) nor acyclic ketene silyl ketals (vide infra) have such reactivity toward alkyl isocyanates.

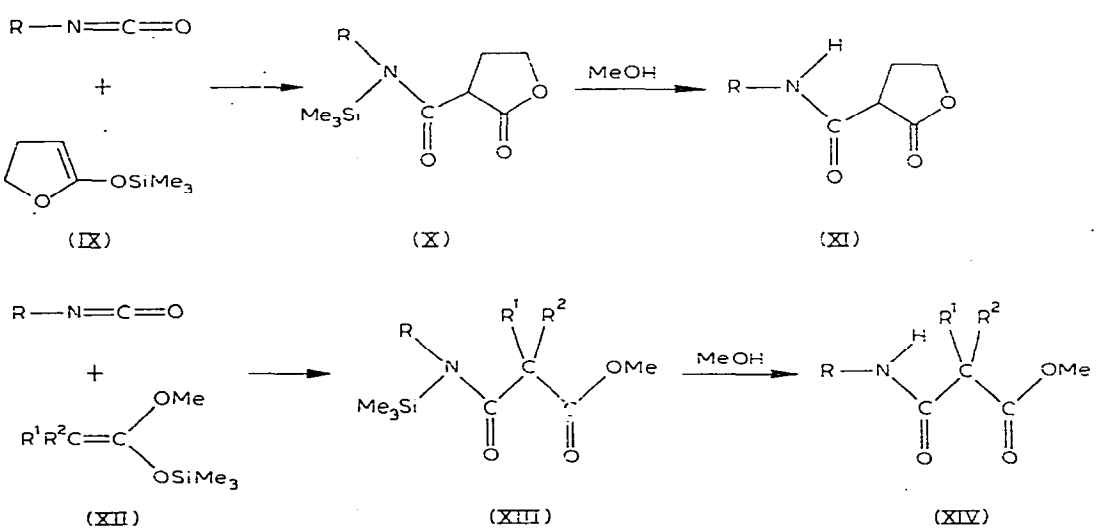


TABLE 6

DATA FOR THE IDENTIFICATION OF 2-(*N*-CARBAMOYL)-γ-BUTYROLACTONE (XI), AND 2-(*N*-CARBAMOYL)ALKANOATES (XIV AND XVI)

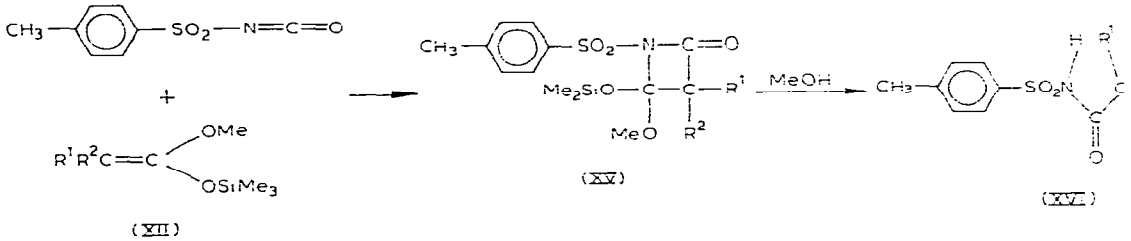
Compound	M.p. (°C) or (b.p. (°C/Torr))	IR (cm^{-1}) [a]				Analysis (found (calcd.) (%))				
		ν(NH)	ν(C=O)	ν(Amide I)	ν(Amide II)	C	H	N	Cl	S
XIa	133—135	3350	1740	1690	1540	54.97 (55.13)	4.21 (4.21)	5.66 (5.86)	14.62 (14.79)	
XIb	74—75	3270	1770	1670	1560 [b]	56.86 (58.80)	6.58 (6.55)	8.22 (8.28)		
XIc	(109/0.2)	3310	1760	1660	1540 [c]	50.37 (50.35)	6.11 (6.34)	9.76 (9.79)		
XIVa	89—90	3250 3180	1720	1660	1540	56.39 (56.37)	5.35 (5.52)	5.32 (5.48)	13.97 (13.87)	
XIVb	78—79	3320	1720	1660	1530	65.18 (65.14)	6.78 (6.83)	6.46 (6.33)		
XIVc	82—83	3250	1750	1650	1540	63.83 (63.76)	6.30 (6.32)	6.87 (6.76)		
XIVa	oil	3250	1755	1730	1440 [c]	58.93 (58.78)	4.99 (4.93)	3.82 (4.03)		9.16 (9.23)
XVIb	oil	3250	1750	1720	1440 [c]	50.29 (50.52)	5.36 (5.30)	4.87 (4.91)		11.14 (11.24)
XVIc	100—101	3340	1750	1715	1420	52.30 (52.16)	5.70 (5.72)	4.63 (4.68)		10.76 (10.71)
XVId	110—112	3250	1750	1725	1425	56.60 (56.62)	6.17 (6.30)	4.06 (4.13)		9.69 (9.48)

[a] Measured as KBr disk. [b] C=C stretching band was observed at 1640 cm^{-1}. [c] Measured as neat liquid.

Ketene silyl ketals derived from open chain alkanoates were found to be less reactive than the cyclic one (IX) and some heating is necessary to promote the reaction with aryl isocyanates. Thus, acyclic ketene silyl ketals (XII) reacted with aryl isocyanates such as *p*-chlorophenyl and phenyl isocyanates at 45—80° C to afford 2-(*N*-silylcarbamoyl)alkanoates (XIII) in moderate to good yields.

The IR spectrum of X or XIII shows both a C=O stretching band in the 1720—1775 cm^{-1} region and an amide I band in the 1640—1660 cm^{-1} region, and no band due to NH stretching. Thus, it is concluded that either X or XIII has the 2-(*N*-trimethylsilylcarbamoyl)alkanoate structure. It should be noted that the nucleophilic addition of ketene silyl ketals proceeds with migration of the trimethylsilyl group from the enol oxygen to the nitrogen of the isocyanate.

In contrast to this, when *p*-toluenesulfonyl isocyanate was used as substrate, [2 + 2]-cycloaddition was observed to proceed, giving 1-(*p*-toluenesulfonyl)-4-siloxyazetidin-2-ones (XV) in high yields.



The β-lactam structure of XV is confirmed on the basis of the fact that the IR spectrum of XV displays only one C=O stretching band in the 1745—1755 cm^{-1} region and no band due to NH stretching. Results and spectral data are listed in Table 5.

The adducts, X and XIII, thus obtained were easily desilylated by methanol at ambient temperature to afford 2-(*N*-substituted carbamoyl)-γ-butyrolactones (XI) and 2-(*N*-arylcarbamoyl)-alkanoates (XIV) respectively, in excellent yields. In a similar manner, the adduct XV was desilylated to give 2-(*N*-*p*-toluenesulfonylcarbamoyl)alkanoates (XVI) in almost quantitative yields. Physical properties and spectral and analytical data are summarized in Table 6.

Experimental

Measurement

Boiling points and melting points were uncorrected. The infrared spectra were measured on a Hitachi EPI-G3 or 285 spectrophotometer using samples as neat liquid or in KBr disks. The nuclear magnetic resonance spectra were obtained using a Varian T-60 or Hitachi R-20B spectrometer with TMS as the internal standard. Analytical gas chromatography (GLC) was carried out on a Shimadzu GC-3BT using a column packed with 3% SE-30 or 3% OV-17.

Materials

Silyl enol ethers were prepared by House's method [13], hydrosilylation of

α,β-unsaturated ketones in the presence of tris(triphenylphosphine)chlororhodium [14], and dehydrogenative condensation of ketones with hydrosilanes in the presence of palladium dichloride/thiophenol [15]. Ketene silyl ketals were prepared by Ainsworth's method [8]. 4,5-Dihydro-2-trimethylsiloxyfuran was prepared by the method reported by Rasmussen and Hassner [16]. Aryl, alkyl and *p*-toluenesulfonyl isocyanates were obtained from commercial sources.

Reaction of silyl enol ethers with aryl isocyanates

A typical procedure is described for the reaction of 1-trimethylsiloxycyclopentene with phenyl isocyanate: A mixture of 1-trimethylsiloxycyclopentene (3.18 g, 20 mmol), phenyl isocyanate (2.38 g, 20 mmol) and 0.1 ml of triethylamine was heated at 130°C for 12 h with stirring under nitrogen. The completion of the reaction was checked by means of IR spectroscopy. The formation of 2-siloxycyclopent-1-enecarboxamide (IIa) was confirmed on the basis of IR and NMR spectra (see Table 2). Then, the reaction mixture was treated with 30% aqueous methanol with stirring for 1 h and subsequently was extracted with ether. The extracts were dried over magnesium sulfate. Evaporation of ether left a solid, which was recrystallized from ether to give colorless prisms of *N*-phenyl-2-oxocyclopentanecarboxamide (IIIa, 3.82 g, 94%).

Results obtained with a variety of cyclic silyl enol ethers (I) and aryl isocyanates are summarized in Table 1. Spectral data of 2-siloxycycloalk-1-enecarboxamides (II) and 2-oxocycloalkanecarboxamides (III) are listed in Table 2. Except IIId, the adducts III are known compounds.

N-α-Naphthyl-2-oxocyclohexanecarboxamide (IIId) Found: C, 76.14; H, 6.35; N, 5.17. $C_{17}H_{17}NO_2$ calcd.: C, 76.38; H, 6.41; N, 5.24%.

Reaction of silyl enol ethers with p-toluenesulfonyl isocyanate

A typical procedure is as follows: 1-Trimethylsiloxycyclopentene (1.56 g, 10 mmol) was added to *p*-toluenesulfonyl isocyanate (1.97 g, 10 mmol) with stirring at ambient temperature. After the exothermic reaction had ceased, stirring was continued for additional 15 min. Then, the resulting colorless needles were washed with n-hexane (5 ml). The obtained crystals of *N*-(*p*-toluenesulfonyl)-2-trimethylsiloxycyclopent-1-enecarboxamide (IVa, 3.42 g, 97%) were pure enough to satisfy elemental analyses.

IVa: Colorless needles, m.p. 73—79°C. Found: C, 54.09; H, 6.49; N, 3.92; S, 9.05. $C_{16}H_{23}NO_4SSi$ calcd.: C, 54.36; H, 6.56; N, 3.96; S, 9.07%.

To IVa (3.0 g) was added methanol (0.5 ml) with stirring. After 30 min, 5 ml of ether was added to form colorless prisms of *N*-(*p*-toluenesulfonyl)-2-oxocyclopentanecarboxamide (Va, 2.34 g, 98%).

In a similar manner, the reactions of open chain silyl enol ethers, VI, with *p*-toluenesulfonyl isocyanate were carried out at ambient temperature. As the resulting adducts, VII, were viscous liquids, they were treated immediately with methanol, without purification, and the methanolysis product was recrystallized from ether to give crystalline *N*-(*p*-toluenesulfonyl)-2-oxoalkanecarboxamides (VIII).

Results are summarized in Table 3. Physical and analytical data for V and VIII are also listed in Table 3. Spectral data for the identification of the adducts IV and VII are listed in Table 4.

Reactions of ketene silyl ketals with aryl, alkyl and p-toluenesulfonyl isocyanates

Typically, a mixture of 4,5-dihydro-2-trimethylsiloxyfuran (IX, 1.58 g, 10 mmol) and *p*-chlorophenyl isocyanate (1.54 g, 10 mmol) was stirred at room temperature for 3 h. Distillation of the reaction mixture gave 2-(*N*-*p*-chlorophenyl-*N*-trimethylsilylcarbamoyl)-γ-butyrolactone (Xa, 2.15 g, 68%).

The reaction of other ketene silyl ketals with aryl isocyanates was carried out at 45—85°C in a similar manner to give the adducts XIII in fairly good yields. Although the structure of X was confirmed on the basis of its IR and NMR spectra, distilled samples of Xa—Xc were not pure enough to satisfy elemental analyses because of their partial decomposition during distillation.

Methyl 2-(*N*-*p*-chlorophenyl-*N*-trimethylsilylcarbamoyl)-2-methylpropionate (XIIIa). Found: C, 54.95; H, 6.48; N, 4.45; Cl, 10.62. $C_{15}H_{22}ClNO_3Si$ calcd.: C, 54.95; H, 6.76; H, 4.27; Cl, 10.81%.

Methyl 2-(*N*-phenyl-*N*-trimethylsilylcarbamoyl)-2-methylpropionate (XIIIb). Found: C, 61.38; H, 7.88; N, 5.05. $C_{15}H_{23}NO_3Si$ calcd.: C, 61.40; H, 7.90; N, 4.77%.

Methyl 2-(*N*-phenyl-*N*-trimethylsilylcarbamoyl)propionate (XIIIc). Found: C, 60.00; H, 7.48; N, 5.11. $C_{14}H_{21}NO_3Si$ calcd.: C, 60.18; H, 7.58; N, 5.01%.

Similarly, the reaction of ketene silyl ketals with *p*-toluenesulfonyl isocyanate was carried out at ambient temperature for 15 min. An exothermic reaction took place to give 1-(*p*-toluenesulfonyl)-4-trimethylsiloxyazetidin-2-ones (XV) in nearly quantitative yields. The azetidinone structure of XV was confirmed on the basis of IR and NMR spectra. Then, XV was treated with methanol without special purification to give crystals of 2-(*N*-*p*-toluenesulfonylcarbamoyl)alkanoates (XVI) in almost quantitative yield.

Results of the reaction of ketene silyl ketals with aryl, alkyl and *p*-toluenesulfonyl isocyanates are summarized in Table 5. Physical and spectral data of the products are also shown in Table 5. Physical properties and spectral and analytical data for 2-(*N*-carbamoyl)-γ-butyrolactones (XI) and 2-carbamoylalkanoates (XIV and XVI) are listed in Table 6.

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References

1 J.K. Rasmussen, Synthesis, (1977) 91 and ref. therein.
2 G. Stork and P.F. Hudrlik, J. Amer. Chem. Soc., 90 (1968) 4462, 4464; H.O. House, M. Gall, and H.D. Olmstead, J. Org. Chem., 36 (1971) 2361; R.M. Coates, L.O. Sandefur and R.D. Smillie, J. Amer. Chem. Soc., 97 (1975) 1619; H.O. House, Modern Synthetic Reactions, W.H. Benjamin, Menlo Park, Calif., 1972, Chapter 9.
3 I. Kuwajima and E. Nakamura, J. Amer. Chem. Soc., 97 (1975) 3257.
4 T. Mukaiyama, K. Banno, and K. Narasaka, J. Amer. Chem. Soc., 96 (1974) 7503; K. Banno and T. Mukaiyama, Chem. Lett., (1975) 741.
5 K. Narasaka, K. Soai, Y. Aikawa, and T. Mukaiyama, Bull. Chem. Soc. Japan, 49 (1976) 779.
6 K. Saigo, M. Osaki and T. Mukaiyama, Chem. Lett., (1975) 989.

7 P.L. Creger, Tetrahedron Lett., (1972) 79.
8 C. Ainsworth, F. Chen, Y.-N. Kuo, J. Organometal. Chem., 46 (1972) 59.
9 As to the preliminary results, see I. Ojima, S. Inaba, and Y. Nagai, Tetrahedron Lett., (1973) 4271; idem., Chem. Lett., (1974) 1069.
10 S. Hünig, Angew. Chem., 71 (1959) 312; G. Opitz and E. Tempel, Ann. Chem., 699 (1966) 74; D.H. Clemens, A.J. Bell, and J.L. O'Brien, J. Org. Chem., 29 (1964) 2923; K. Matterstock and H. Jensen, Ger. Pat., (1964) 1, 160, 432; Chem. Abstr., 60 (1964) 9247f.
11 F. Effenberger and R. Gleiter, Angew. Chem., 75 (1963) 450; idem., Chem. Ber., 97 (1964) 1576; F. Effenberger and G. Kiefer, Angew. Chem., 79 (1967) 936; R. Lattrell, Ann. Chem., 722, (1969) 132.
12 S. Hünig, K. Hübner, and E. Benzing, Chem. Ber., 95 (1962) 926.
13 H.O. House, L.J. Czuba, M. Gall and H.D. Olmstead, J. Org. Chem., 34 (1969) 2324.
14 I. Ojima, T. Kogure, M. Nihonyanagi, and Y. Nagai, Bull. Chem. Soc. Japan, 45 (1972) 3506.
15 Y. Nagai, K. Uetake, T. Yoshikawa and H. Matsumoto, J. Syn. Org. Chem. Japan, 31 (1973) 759.
16 J.K. Rasmussen and A. Hassner, J. Org. Chem., 39 (1974) 2558.
17 R.J. Brown, F.W.S. Carver, and B.L. Hollingsworth, J. Chem. Soc., (1961) 4295.